Atmospheric Environment 181 (2018) 61–69

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Historical sources of black carbon identified by PAHs and $\delta^{13}C$ in Sanjiang Plain of Northeastern China

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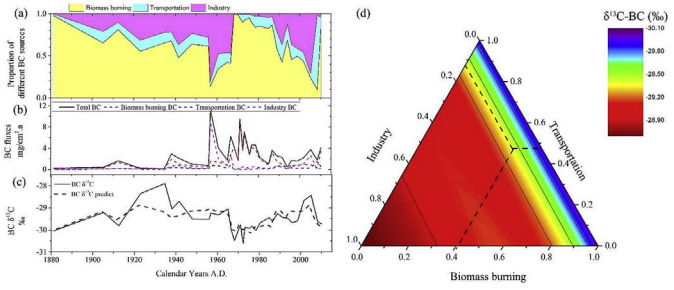
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Black carbon
PAHs
$\delta^{13}C$-BC
Sanjiang plain

ABSTRACT

Black carbon (BC), the byproduct of incomplete combustion of fossil fuels and biomass can be stored in soil for a long time and potentially archive changes in natural and human activities. Increasing amounts of BC has been produced from human activities during the past 150 years and has influenced global climate change and carbon cycle. Identifying historical BC sources is important in knowing how historical human activities influenced BC and BC transportation processes in the atmosphere. In this study, PAH components and $\delta^{13}C$-BC in peatland in the Sanjiang Plain were used for identifying and verifying regional BC sources during the last 150 years. Results showed that environment-unfriendly industry developed at the end of the 1950s produced a great amount of BC and contributed the most BC in this period. In other periods, however, BC in the Sanjiang Plain was mainly produced from incomplete biomass burning before the 1990s; particularly, slash-and-burn of pastures and forests during regional reclamation periods between the 1960s and 1980s produced a huge amount of biomass burning BC, which then deposited into the surrounding ecosystems. With the regional reclamation decreasing and environment-friendly industry developing, the proportion of BC emitted and deposited from transportation sources increased and transportation source became an important BC source in the Sanjiang Plain after the 1990s.

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https://doi.org/10.1016/j.atmosenv.2018.03.026
Received 19 August 2017; Received in revised form 21 January 2018; Accepted 11 March 2018
Available online 12 March 2018
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1. Introduction

Black carbon (BC) is produced by the incomplete combustion of fossil fuels and biomass (Hammes et al., 2007) and co-emitted with polycyclic aromatic hydrocarbons (PAHs) or other organic pollutants from natural or anthropogenic sources (Ray et al., 2012). As an important component of the atmospheric aerosol, BC is capable of negatively affecting human health and changing the climate (Ramanathan and Carmichael, 2008; Galdos et al., 2013). After a few days of staying and transporting in the atmosphere, BC generally deposits into soils and stores in the soil carbon pool for thousands of years (Cape et al., 2012; Lehndorff et al., 2014). Recently, BC fluxes in sediment archives (e.g. lake, peat) were widely used for reconstructing historical regional BC emission and evaluating the degree of natural and anthropogenic factors influencing BC production (Cong et al., 2013, 2016; Gao et al., 2014; Ruppel et al., 2015).

Identifying sources of BC is helpful in better understanding the proportion of different BC sources and the influence of regional climate change and human activities on BC fluxes (Lehndorff et al., 2015; Sun et al., 2017). Radioactivity of carbon isotope (^{14}C) in BC from ancient fossil fuels or modern biomass and stable carbon isotope (^{13}C) from different vegetation burning (i.e. C3 and C4 vegetation) could be used for identifying BC sources in aerosol and sediments (Chen et al., 2013; Wang et al., 2013a). Δ^{13}C-BC in particles during coal burning were from −23‰ to −25‰ and most of the other fossil fuel burning particles were within −23 to −27‰ (Widory, 2006; López-Veneroni, 2009, Table 1). Glaser et al. (2005) reported that values of δ^{13}C from vehicle soot were from −22‰ to −25‰ and between −24‰ and −26‰ in coal soot. Δ^{13}C-BC produced during biomass burning is always related to δ^{13}C in original biomass. Biomass burning process resulting in δ^{13}C-BC values in residual were lower than those in origin biomass by −2‰ to −6‰ (Saiz et al., 2015). For calculating biomass components based on δ^{13}C in biomass, −27‰ and −13‰ were assumed as specific values for C3 woody biomass and C4 grass biomass respectively (Cerling et al., 1997). Although the δ^{13}C values in modern char were from −27‰ to −29‰ and lower than those in fossil char, ranging from −24‰ to −27‰ (Gierga et al., 2014), δ^{13}C-BC from C3 plant burning sources were lower than −27‰ in general (Bird and Ascough, 2012; Saiz et al., 2015). In summary, δ^{13}C-BC values from solid fossil fuel burning were from −23‰ to −26‰ which were slightly higher than those from C3 vegetation burning (−27‰ to −33‰).

Although values of δ^{13}C from C3 vegetation burning were relatively lower than those from solid fossil fuel combustion, δ^{13}C-BC values from liquid fossil fuel burning were from −22‰ to −30‰, which means it is difficult to identify the sources of BC by δ^{13}C-BC alone after humans started to heavily use liquid fossil fuels. PAH components varied with different burning sources and were successfully used to identify burning sources based on PAH components produced in a number of studies (Yunker et al., 2002; Pontevedra-Pombal et al., 2012). PAHs were always co-emitted with BC during fossil fuel combustion and biomass burning (Agarwal and Bucheli, 2011); thus, burning sources identified by PAH components could also be used to indicate pyrolysis carbon sources (Mitra et al., 2002; Wang et al., 2014). A combination of PAHs sources in sediments identified by PAH components with δ^{13}C-BC technique should be demonstrated use in identifying the historical BC sources in sediment archives.

Peatlands with and continuous inputs by deposition can provide ideal archives of BC and PAHs for reconstructing historical BC fluxes and sources (Martini et al., 2007; Gao et al., 2014). Because slow rates of decomposition under anaerobic conditions, the degradation rates of PAHs and BC were much lower than other ecosystems and the impact of different degradation rates of PAHs on PAH components in peatland could be ignored. The Sanjiang Plain, located in the northeast of China, is the main wetland distribution region in China (Wang et al., 2009). Since 1895, the Qing government began to allow people from Southern China to migrate into this region and reclaim lands (Zhang et al., 2006). The population in the Heilongjiang Province increased by 30 times from 1.27 million in 1897 to 38.34 million in 2011 (Li and Yuan, 1996; Statistics Office of Heilongjiang Province, 2012). As a result, the effects of human activity were extremely prevalent during the last 100 years. The area of arable land increased by 2.5 times from 1954 to 2005; the region has become one of the most important land areas for crops (55%) in China (Wang et al., 2009). Slash-and-burn of pastures and forests during reclamation and regional economic development emitted a large amount of BC and caused a great increase in BC fluxes during the last 150 years (Gao et al., 2014). Because of the great changes in BC emissions due to the increasing human population and intensity of human activities during the last 150 years, the Sanjiang Plain is an ideal study area to analyze the relationship between human activities and BC fluxes.

In a previous study (Gao et al., 2014), BC fluxes in the SJD peat core were reconstructed and used primarily for focusing on the relationship between regional BC fluxes and regional economic development. However, it is unclear which local BC sources led to the sharp increases in BC fluxes during several special periods (e.g. around 1960s). In order to reveal the controlling factors of high BC fluxes in these special periods, δ^{13}C-BC and PAH components were analyzed in the same peat core samples to identify BC sources in the present study. Based on the discriminant analysis, the proportions of BC from different sources were identified by PAH components and the BC emissions from different sources were calculated. Δ^{13}C-BC predicted by general additives models based on the proportion of BC sources were used to compare with δ^{13}C-BC from different BC sources reported in previous studies and evaluate whether we could use PAH components identify BC sources. By comparing the history of local economic development, the relationship between local economic development and BC fluxes from different sources in Sanjiang Plain were determined.

Table 1
Literature δ^{13}C-BC for pyrogenic carbon sources.

Sources	Classified	δ^{13}C-BC	Reference
Solid fossil fuel (coal)	Industry	−23‰ to −25‰	Widory, 2006
coal soot	Industry	−24‰ to −26‰	Glaser et al., 2005
Industry		−23‰ to −26‰	
Liquid fossil fuel (Fuel oil)	Transportation	−27‰ to −30‰	Widory, 2006
vehicle soot	Transportation	−22‰ to −25‰	Glaser et al., 2005
Diesel/gasoline vehicle soot	Transportation	−23‰ to −26‰	López-Veneroni, 2009
Transportation		−22‰ to −30‰	
C4 grass biomass	Biomass Burning	−15‰ to −19‰	Cerling et al., 1997; Saiz et al., 2015
C3 woody biomass	Biomass Burning	−29‰ to −33‰	Cerling et al., 1997; Saiz et al., 2015
C3 plants	Biomass burning	< −27‰	Bird and Ascough, 2012
C3 biomass burning		−27‰ to −33‰	

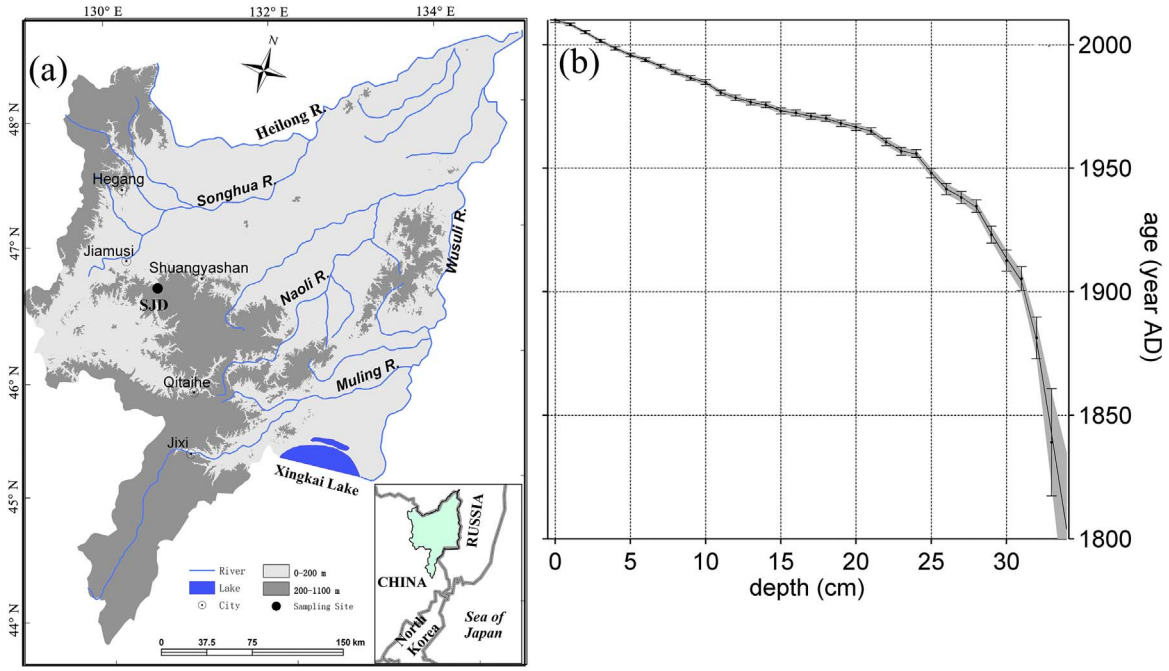

Fig. 1. (a) Location of SJD peat core in Sanjiang Plain, northeast of China; (b) Depth versus age plot calculated by the CRS model, the grey shadow means the 95% confidence intervals of depth-age model (Gao et al., 2014).

2. Materials and methods

2.1. Site description and sampling

The Sanjiang Plain is both the major rice production region and wetlands distribution region, with more than 80% of the wetlands converted into farmland during the last 60 years (Wang et al., 2009). Peat samplings were carried out in undisturbed peatlands in the Sanjiang Plain, Northeast China (Fig. 1a). SJD peatland (46°34.864′ N; 130°39.873' E) is located in the valley zone between Zhangguangcai ridge and Wanda Mountain, with an annual mean temperature of 2.4 °C and annual mean precipitation 550 mm. The local plant communities in the sampling sites are part of the *Betula fruticosa-Calamagrostis angustifolia* community. In Nov 2010, peat cores were collected and sliced into 0.01 m sections using a stainless steel knife; samples were stored in sealed polyethylene plastic bags and brought to the lab for further analysis. Samples were loosely disaggregated to facilitate air-drying at 20 °C. The age-depth model (Fig. 1b) were calculated in a previous study (Gao et al., 2014).

2.2. Chemical analysis

2.2.1. PAHs

Details of PAHs methods were shown in a previous study (Cong et al., 2016). Briefly, 20 g peat samples combined with Na_2SO_4 (20 g) were extracted with 20 ml of hexane–acetone (1:1, v/v) at 20 °C under ultrasonication. The extract was then concentrated and solvent-exchanged with hexane in a rotary evaporator. The separation was performed with a Na_2SO_4-silica gel-Na_2SO_4 column under 40 mL pentane solvent leaching. PAHs were eluted with hexane–dichloromethane (2:3, v/v) after aliphatic ethers had been removed with pentane. The elution solution was again concentrated, solvent-exchanged with hexane comma and blown to 1 ml. The instrumental analysis was performed with a GC/MS system (QP5050A). The SEPA Institute standard samples of 16 priority PAH standard mixtures were adopted as external standards for quantitative analysis, and the recovery rates were around 80–110%.

2.2.2. Δ^{13}C-BC

To determine the δ^{13}C-BC, we used the dichromate oxidation method, and all other forms of carbon were removed from the samples (1 g dry peat soils) using treatments of HCl, NaOH and a mixture of $K_2Cr_2O_7$ and H_2SO_4 in a water bath at 55 °C (Gao et al., 2014). After pretreatment of samples, the residual carbon as BC and δ^{13}C in residual carbon as δ^{13}C-BC were quantified by using a continuous-flow isotope ratios mass spectrometer (CF-IRMS) at the Analysis and Test Center of Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. The CF-IRMS system consists of an EA (Flash, 2000 series) coupled to a Finnigan MAT 253 mass spectrometer. The combustion temperature was set at 960 °C. BC reference material (charred wood) produced in the Department of Geography at the University of Zurich (Hammes et al., 2006) was used to verify the method of measuring BC in the peat soils. Standard samples with known carbon contents and carbon isotope ratios (IRMS certified reference: BN/132 357) were used to calibrate the measurement and to monitor the working conditions. Carbon isotope ratios (δ^{13}C) were expressed relative to Pee Dee Belemnite (δ^{13}C designated 0.0‰)

2.3. Data processing and modeling

2.3.1. Discriminant analysis

Discriminant analysis (i.e. linear discriminant analysis) is a method of linear model which could not only group the data set into the known grouping of the objects like cluster analysis also could interpret the meaning of these groups (Legendre and Legendre, 2012). Similar with multiple linear regression and canonical correlation analysis, discriminant analysis tests for differences in the predictor variables among the known groups (i.e. PAH components in different sources) using Wilks' lambda and find the linear combinations of the predictors that best discriminate among the groups. Based on linear combinations, assess the relative contributions of the known groups to unknown groups (i.e. PAH components in different periods) and calculate the contribution rates according to the distance of scores between predictor variables and known group (Legendre and Legendre, 2012). Based on the discriminant analysis, all PAH components in peat core and different sources, we identified the contribution rates of different PAHs

sources to total PAHs (i.e. BC) in peat cores in different periods. In order to quantitatively describe the BC and PAHs sources, the characters of PAHs in different sources were selected and used by the following studies: transportation fossil fuel burning (Khalili et al., 1995; Kim Oanh et al., 1999; Marr et al., 1999; Kim Oanh et al., 2002; Chen et al., 2005; He et al., 2010), industry fossil fuel burning (Khalili et al., 1995; Lee et al., 2004), and biomass open burning (Jenkins et al., 1996; Zhang et al., 2008). Other sources were divided based on which the types of fossil fuels consumption (i.e. solid fossil fuels belong to industry source and liquid fossil fuels belong to transportation source). The contribution ratios of different PAHs sources were used to indicate the contribution ratios of different BC sources to BC fluxes in SJD peat core during the last 150 years. All discriminant analysis calculations were performed using SPSS 20.0 (SPSS, Inc.).

2.3.2. General additives models (GAMs)

GAMs are regression models where smoothing splines were used for covariates (Hastie and Tibshirani, 1990) and have been widely used in handling the complex non-linearity relationship (Pearce et al., 2011; Gao et al., 2014). In the present study, GAMs were used for modeling the relationship between δ^{13}C-BC and different BC source contribution rates which identified by PAH components and predicting the δ^{13}C-BC based on the different BC source contribution rates. The δ^{13}C-BC predicted by different BC sources and the δ^{13}C-BC reported in previous studies were compared and used to evaluate whether BC sources could be identified by PAH components. Smoothing parameters were selected by generalizing cross-validation (GCV) in semi-parametric regression; the residual distribution was assumed to be Gaussian distribution (Wood, 2011). This model was conducted by using the 'gam' function in the R environment for statistical computing (Team, 2015) with the package 'mgcv' (Wood, 2011).

3. Results

3.1. Variation of δ^{13}C-BC

The range of δ^{13}C-BC variation in the peat core were from −30.6‰ to −27.9‰ (Fig. 2). The δ^{13}C-BC at the 29 cm layer was −27.9‰ and the highest in the peat core; the lowest δ^{13}C-BC was −30.6‰ and appeared at the 17 cm layer. Δ^{13}C-BC increased from −30.0‰ at the bottom peat soils to −27.9‰ at the 28–29 cm layers, and then decreased from 29 cm to 17 cm. From 17 cm to top layers of the peat profile, the δ^{13}C-BC obvious increased from −30.6‰ to −28.5‰. By comparing to the age-depth model, highest δ^{13}C-BC appeared in the 1900–1950, and increased from the 1970s to present.

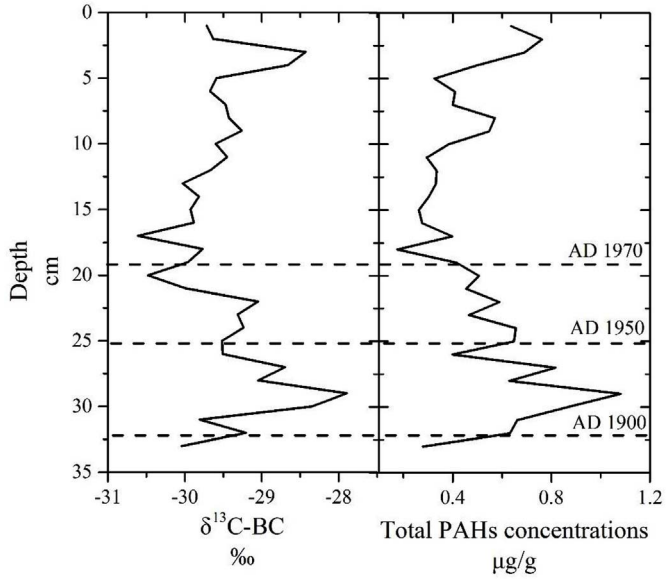

Fig. 2. Variation of total PAHs concentrations and BC-δ^{13}C with depth in SJD peat core.

3.2. PAHs concentrations

Based on human activities history in Sanjiang Plain, four periods were divided during the last 150 years (i.e. before 1900, 1900–1950, 1950–1970, and after 1970). Average concentration (μg/g) and standard deviation of PAHs in different periods were shown in Table 2. The range of total PAHs concentrations in SJD peat cores were between 0.18 and 1.08 μg/g, showing similar variation trends with δ^{13}C-BC (Fig. 2). Highest concentrations of total PAHs concentrations appeared at the 28–29 cm layers, which was accumulated in the 1930s. From the 1930s–1970s, total PAHs concentrations decreased from 1.08 to 0.18 μg/g. From the 1970s to present, total PAHs concentrations were relatively stable and lower than other periods. In the depth of peat layers which lower than 5 cm, total PAHs concentrations increased to 0.76 μg/g and were slightly lower in the surface (0–1 cm) peat soils (0.64 μg/g).

3.3. PAHs fluxes and diagnostic ratios

Total PAHs fluxes and three PAHs diagnostic ratios during the last 150 years are shown in Fig. 3. Before the 1930s, the total PAHs fluxes were relatively stable and lower than 500 μg/m^2. a. After the 1930s, total PAHs fluxes started increasing; the highest fluxes were more than 1 500 μg/m^2 and appeared in the 1950s. After the 1960s, PAHs fluxes decreased to about 600 μg/m^2. a. The ratios of Ipy/(Ipy + Bpe) were around 0.5 before the 1970s, and lower than 0.5 after the 1970s. Around the 1960s, the ratios of Ipy/(Ipy + Bpe) were higher than other periods. The ratios of BaA/(BaA + Chr) fluctuated between 0.15 and 0.2 before the 1970s. From the 1970s to the present, however, the ratios of BaA/(BaA + Chr) were higher than 0.2. The ratios of Flt/(Flt + Pyr) in SJD peat core were higher than 0.5 during the last 150 years.

4. Discussion

4.1. BC sources revealed by PAH components

Because BC and PAHs were always co-emitted from the same pyrolysis sources, the proportion of different PAHs sources could also be used to estimate the proportion of pyrolysis sources (i.e. BC sources). The diagnostic ratios of PAHs are useful for indicating the sources of PAHs (Yunker et al., 2002; Bucheli et al., 2004), The ratios of Flt/(Flt + Pyr) > 0.5 suggest that PAHs were generally from biomass burning; ratios from 0.4 to 0.5 mean that biomass burning and fossil fuel (e.g. diesel, gasoline and coal) consumption resulted in the mixed sources of PAHs. If the PAHs were emitted mostly from petroleum sources, both ratios of BaA/(BaA + Chr) and Ipy/(Ipy + Bpe) would be lower than 0.2; ratios of BaA/(BaA + Chr) > 0.35 and Ipy/(Ipy + Bpe) > 0.5 mean that the major PAHs sources were from biomass burning (Yunker et al., 2002). In the present study, historical variation of PAHs diagnostic ratios in SJD peat core were shown in Fig. 3.

Although the ratio of Flt/(Flt + Pyr) in SJD peat core slightly increased from 0.70 to 0.75 before the 1940s and decreased from 0.75 to 0.60 thereafter, it was still much higher than 0.5 during the last 150 years. Based on the ratios of Flt/(Flt + Pyr) solely, the sources of PAHs (BC) could have all been from biomass burning sources. Similarly, the ratios of Ipy/(Ipy + Bpe) > 0.5 in two periods (i.e. before the 1900s and around the 1960s) further suggest that biomass burning was the major source in these periods. However, in other periods, the ratios of Ipy/(Ipy + Bpe) were between 0.3 and 0.5, which means the PAHs (BC) in these periods were from the mixture of biomass burning and liquid fossil fuels combustion. Fluctuation of ratios of BaA/(BaA + Chr)

Table 2
Average concentration (μg/g) and standard deviation of PAHs in different periods.

	Before 1900 (n = 2)		1900–1950 (n = 7)		1950–1970 (n = 7)		After 1970 (n = 18)		Total (n = 34)	
	Average (μg/g)	Standard Deviation	Average (μg/g)	Standard Deviation	Average (μg/g)	Standard Deviation	Average (μg/g)	Standard Deviation	Average (μg/g)	Standard Deviation
NaP	0.0783	0.0413	0.1240	0.0607	0.0690	0.0207	0.1464	0.0551	0.1218	0.0583
Any	0.0058	0.0002	0.0073	0.0020	0.0070	0.0023	0.0094	0.0031	0.0083	0.0029
Ana	0.0060	0.0002	0.0091	0.0022	0.0083	0.0011	0.0090	0.0036	0.0087	0.0029
Flu	0.0370	0.0022	0.2037	0.0581	0.1504	0.0777	0.0368	0.0127	0.0946	0.0837
Phe	0.1093	0.0084	0.2681	0.0752	0.2229	0.0442	0.0953	0.0278	0.1579	0.0868
Ant	0.0044	0.0003	0.0069	0.0022	0.0055	0.0012	0.0046	0.0017	0.0053	0.0018
Flt	0.0305	0.0029	0.0582	0.0175	0.0411	0.0139	0.0344	0.0122	0.0405	0.0161
Pyr	0.0134	0.0005	0.0173	0.0048	0.0140	0.0052	0.0183	0.0101	0.0169	0.0081
BaA	0.0018	0.0003	0.0029	0.0012	0.0017	0.0008	0.0048	0.0037	0.0036	0.0030
Chr	0.0069	0.0010	0.0138	0.0056	0.0074	0.0033	0.0162	0.0110	0.0133	0.0092
BbF	0.0020	0.0004	0.0033	0.0013	0.0019	0.0009	0.0094	0.0086	0.0061	0.0071
BkF	0.0018	0.0005	0.0057	0.0055	0.0021	0.0009	0.0087	0.0079	0.0063	0.0068
BaP	0.0005	0.0001	0.0025	0.0035	0.0006	0.0004	0.0105	0.0281	0.0062	0.0207
Ipy	0.0006	0.0003	0.0012	0.0009	0.0008	0.0004	0.0069	0.0073	0.0041	0.0061
Dba	0.0004	0.0001	0.0007	0.0008	0.0006	0.0010	0.0024	0.0025	0.0016	0.0021
Bpe	0.0005	0.0000	0.0020	0.0016	0.0007	0.0004	0.0091	0.0101	0.0054	0.0083
Total	0.2994	0.0291	0.7268	0.2172	0.5339	0.0972	0.4220	0.1613	0.5006	0.2015

Abbreviations of PAHs: NaP, Naphthalene; Any, Acenaphthylene; Ana, Acenaphthene; Flu, Fluorene; Phe, Phenanthrene; Ant, Anthracene; Flt, Fluoranthene; Pyr, Pyrene; BaA, Benzo(*a*)anthracene; Chr, Chrysene; BbF, Benzo(*b*)fluoranthene; BkF, Benzo(k)fluoranthene; BaP, Benzo(*a*)pyrene; Ipy, Indeno(1,2,3-*cd*)pyrene; Dba, Dibenzo(a,h)anthracene; Bpe, Benzo(g,hi)perylene.

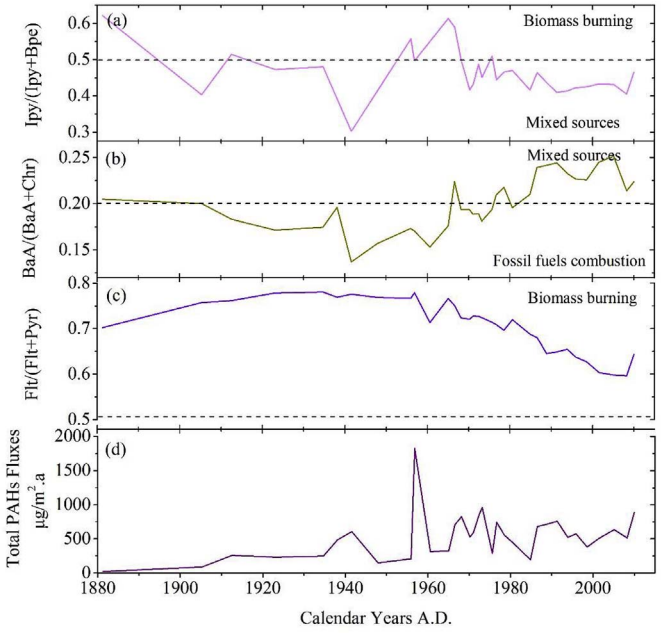

Fig. 3. Variation of ratios of Ipy/(Ipy + Bpe), BaA/(BaA + Chr) and Flt/(Flt + Pyr) as well as total PAHs fluxes in SJD peat core. The dashed lines indicated the boundaries for source assignments of PAHs were based on Yunker et al. (2002).

around 0.2 during the last 150 years and also indicates that the PAHs (BC) were mainly from petrogenic sources or fossil fuels combustion sources. Although the PAHs diagnostic ratios indicate that the pyrolysis products (i.e. PAHs and BC) in SJD could have been mainly from biomass burning or mixed sources, the three selected PAHs diagnostic ratios sometimes revealed contradictory source identification. One potential factor cause these contradictory sources may the changing of different source proportions lead the changing rates of PAHs diagnostic ratios different, and PAHs diagnostic ratios could not identify the changing of several source proportions solely when the PAHs were mainly from mixed sources. For example, the ratios of Flt/(Flt + Pyr) could not identify the changing of fossil fuels combustion source proportion, and the ratios of BaA/(BaA + Chr) could not identify the changing of biomass burning source proportion. However, historical PAHs and BC in SJD peat core were most likely from mixed sources, solely relying on changes in the variation of PAHs diagnostic ratios are insufficient to identify historical PAHs mixture sources and quantify the proportion of different pyrolysis sources.

Discriminant analysis could assess the relative contributions of the known groups (i.e. PAH components in different sources) to unknown groups (i.e. PAH components in SJD peat core) and calculate the contribution rates of different known groups (i.e. different PAHs sources) (Legendre and Legendre, 2012). A number of studies on different components of PAHs from several special sources (Sandercock and Du Pasquier, 2003; Wang et al., 2013b) suggest that the information of PAH components in different sources (i.e. known group) were suitable for discriminant analysis to identify PAHs sources and quantify the contribution rates of different PAHs sources. In the present study, sources of PAHs were divided into three groups, i.e. biomass burning, industry fossil fuel consumption and transportation combustion. According to the characters of biomass burning for residental living, plant and wood burning are included into the biomass burning group; Coals and other fossil fuels burning were included in industry sources. Based on discriminant analysis, the contribution ratios of three pyrolysis sources in SJD peat core during the last 150 years are shown in Fig. 4a. The discriminant results show that biomass burning sources were the main sources of pyrolysis products in SJD peat core during the last 150 years and similar to the results revealed with PAHs diagnostic ratios. Before the 1950s, the contribution rates of industry and transportation sources of pyrolysis products increased and reached the highest proportion of industry sources in the middle of the 1950s. In the 1950s, the pyrolysis products in the Sanjiang plain were mainly from industry sources. And then, the proportion of biomass burning sources increased and contributed the most BC from the 1960s to the 1990s. After the 1990s, the contribution of industry and transportation sources increased again, and became the main BC sources in Sanjiang Plain.

Sources of pyrolysis products identified by discriminant analysis were similar with those revealed from PAHs diagnostic ratios. However, discriminant analysis could decrease the error caused by single PAH component and quantify the proportion of different sources much clearer than PAHs diagnostic ratios. Especially for identify historical sources of pyrolysis products in sediments which were mainly from mixed sources, the proportion of different sources quantified by discriminant analysis could help researchers reconstruct historical sources

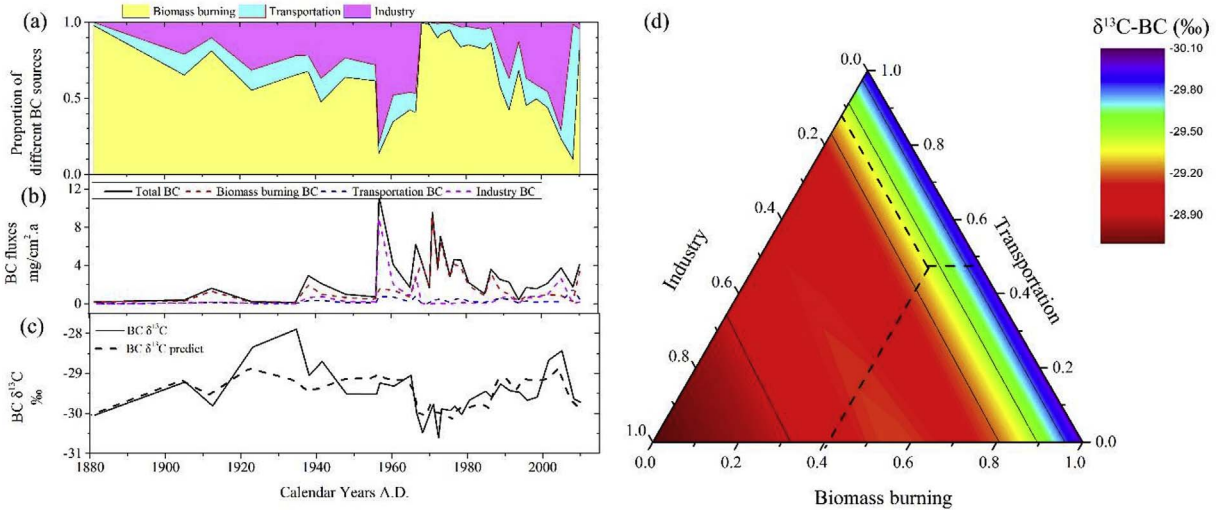

Fig. 4. (a) Historical proportion of pyrolysis sources obtained by discriminant analysis and PAHs components in SJD peat core; (b) Historical variation of BC fluxes from different sources in SJD peat core; (c) Historical variation of origin BC-δ^{13}C (solid line) and BC-δ^{13}C (dashed line) which predicted by GAM model and pyrolysis sources proportion; (d) Relationship between BC-δ^{13}C and the proportions of different sources, the dashed lines indicated the values of BC-δ^{13}C predicted by GAM model with one kind of proportion of different sources.

of pyrolysis products more clearly. Unlike PAHs diagnostic ratios, all PAH components were used in discriminant analysis and decrease the errors on the final results caused by single component of PAHs as far as possible. In all, discriminant analysis is better than normal PAHs diagnostic ratios to identify the proportion of different PAHs sources from mixed products and used for revealing contribution rates of historical PAHs sources in sediments.

4.2. Variation of δ^{13}C-BC and environment implication

Δ^{13}C-BC values are specifically influenced by original combusted materials and could additionally be used for indicating BC sources. If the BC were from a mixture of C3 plants burning and fossil fuels consumed, high δ^{13}C-BC could indicate that more BC were resulted from fossil fuels consumed (Table 1). In this study, δ^{13}C-BC predicted by GAMs and different pyrolysis sources contribution rates which identified by PAH components were used to compare with δ^{13}C-BC from different BC sources and verify whether BC sources could be identified by PAH components (Fig. 4c and d). What's more, little studies had been conducted to distinguish δ^{13}C-BC produced by transportation or industry sources (Glaser et al., 2005; López-Veneroni, 2009); based on pyrolysis products sources identified by PAH components, GAMs were also used in this study for testing whether different fossil fuels consumed could influence the δ^{13}C-BC.

Increases in δ^{13}C-BC values in SJD before the 1940s indicate that the proportion of biomass burning sources decreased and industry sources increased during this period. This is supported by those revealed by PAH components. Around the 1970s, the values of δ^{13}C-BC were lowest and similar to those at the beginning of the 1900s, suggesting that the biomass burning sources were the major BC sources during this period. Similarly, PAH components indicate comparable results. Variation of δ^{13}C-BC predicted by GAM and proportion of different sources generally had similar trends with the actually measured δ^{13}C-BC except those between the 1920 and 1940s. Prediction of δ^{13}C-BC values based on pyrolysis sources identified by PAH components were stable, however, the real δ^{13}C-BC peaked during this period.

The relationship between pyrolysis sources and δ^{13}C-BC shows that the industry and biomass burning sources were two major factors that control the values of δ^{13}C-BC. With the values of δ^{13}C-BC decreasing, the proportion of biomass burning sources increased and the industry or transportation sources decreased (Fig. 4d). When the proportion of biomass burning sources was relatively stable, the δ^{13}C-BC decreased accompanied with the proportion of transportation sources increasing. And when proportions of industry sources were stable, the δ^{13}C-BC decreased with the proportion of biomass burning sources increasing. Based on GAM analysis, the δ^{13}C-BC from transportation sources was around −29.9‰, in the middle of industry and biomass burning sources. The order of δ^{13}C-BC values from different sources predicted by GAM in the present study is industry sources < transportation sources < biomass burning sources, and the order is similar to direct analysis results from previous studies (Glaser et al., 2005; Bird and Ascough, 2012; Gierga et al., 2014).

Although, the values of δ^{13}C-BC could be used to identify historical BC sources in peat cores, δ^{13}C-BC values from transportation sources overlap the other two sources, therefore, it is also difficult to identify the historical transportation sources proportion trend solely based on the δ^{13}C-BC values. Historical trend of δ^{13}C-BC values in peat cores could be used effectively for identifying the historical proportion of industry sources and biomass burning sources. In general, δ^{13}C-BC predicted by pyrolysis source proportions which identified by PAH components are similar with δ^{13}C-BC in direct analysis results in different sources means BC sources could be identified by PAH components. And a combination of δ^{13}C-BC and PAH components calculated by discriminant analysis can be more effectively used for identifying pyrolysis products sources in peat core during the last 150 years.

4.3. Influence of regional economic development on BC fluxes

It is hard to identify local BC sources based on BC fluxes directly (Gao et al., 2014). In the present study, based on the proportion of different BC sources and total BC fluxes, BC fluxes from different sources in different periods were calculated and shown in Fig. 4b. Before the 1950s, BC fluxes from transportation sources were relatively stable with two peaks around the 1910s and the 1940s, and increased obviously after the 1960s. After the 2000s, BC fluxes from transportation sources increased sharply with a clear peak. Around the 1910s, the peak of BC fluxes resulted from increasing fluxes of biomass burning sources. However, BC fluxes from all three types of BC sources increased around the 1940s led to an obvious peak of total BC fluxes in that period. In addition, two obvious peaks appeared in the 1950s and 1970s; in the 1950s, BC fluxes from industry sources increased obviously and was the major cause to the peak of total BC fluxes in this period. However, BC fluxes from increased biomass burning resulted in a peak of total BC fluxes after the 1960s. After the 1960s, biomass burning sources were the main sources of BC in SJD and controlled the total BC fluxes. After the 1980s, BC fluxes from biomass burning sources

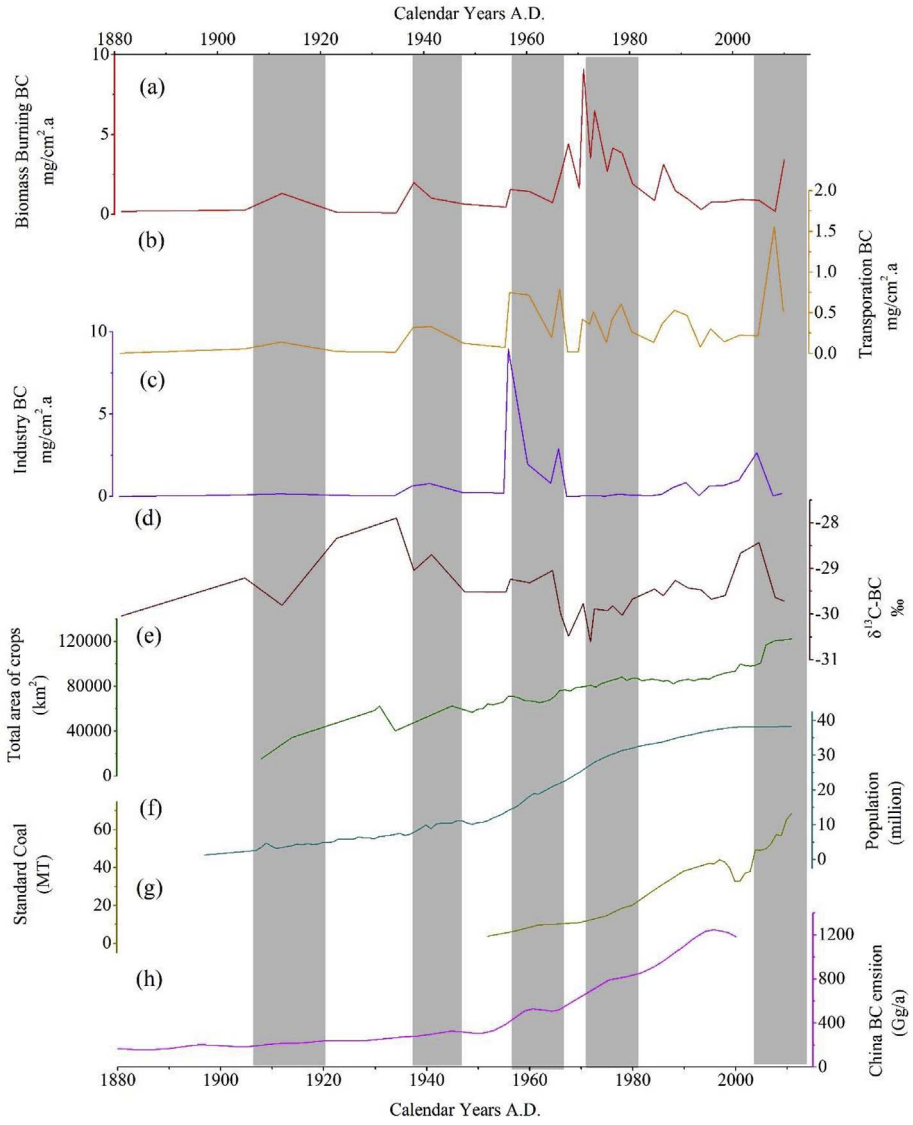

Fig. 5. Historical variation of BC fluxes (Gao et al., 2014) from different sources (a–c) and BC-$\delta^{13}C$ (d) in SJD peat core; Historical total area of crops (e), population (f), consumption of standard coals (g) in Heilongjiang Province (Xu, 1993; Li and Yuan, 1996;; Zhang et al., 2006; Statistics Office of Heilongjiang Province, 2012) and BC emissions in China (h) (Bond et al., 2007).

decreased and the increased BC fluxes were primarily from industry and transportation sources.

In order to reveal how human activities influenced BC fluxes from different sources, BC fluxes from different sources and different regional human activities proxies were compared in Fig. 5. Similar with a previous study (Gao et al., 2014), population, area of crops, standard coal consumed in Heilongjiang province were used as the degree of local human activities to interpret their influence on the sources of BC; in addition, China BC emission was used as regional background of BC emission in this study (Fig. 5). At the beginning of the 1900s, the Qing government started to allow people in the middle and south of China to immigrate into the northeast of China and convert natural ecosystems into farmland (Zhang et al., 2006). This was the first period that humans started to reclaim and covert natural ecosystem (e.g. wetland, forest) to farmland in the Sanjiang Plain, as a result, the area of farmland has increased steadily since 1900s. Increases in BC fluxes from biomass burning sources led total BC fluxes to increase at the beginning of the 1900s. Furthermore, around the 1940s, BC fluxes from all three sources increased, and led a great increase in the total BC fluxes. In this period, the Sanjiang Plain was invaded and controlled by the Japanese army during the Second World War (Zhang et al., 2006); large amount of coals and other natural resources were exploited and transported, raising BC emission from industry and transportation sources. Increase in regional population and farmland area additionally led biomass burning to increase as well. With the intensity of regional human activities increasing, BC fluxes increased greatly in this period.

In the 1950s, the crops area were stable and standard coals consumption increased for developing the regional industry. Especially at the end of the 1950s, the policy of the Great Leap Forward aiming to rapidly develop the country through rapid industrialization and collectivization was implemented in China and a huge number of small steel plants were established and operated during that period (Jiang, 2014). BC emission from these environment-unfriendly steel plants increased sharply and industry sources became the major sources of BC in that period. Huge amounts of BC emission from industry during the Great Leap Forward period led to the highest BC fluxes during the last 150 years in the Sanjiang Plain. After the Great Leap Forward period finished in the 1960s, more than 100′000 soldiers migrated to the Sanjiang Plain as farmers to reclaim wetlands and other types of natural ecosystems into farmland in 1958 (Wang, 2013). The area of crops in the Heilongjiang province increased significantly at the beginning of the 1960s, accompanying a great increase in BC fluxes from biomass

burning sources. After the Great Leap Forward period finished, BC emitted from industry sources decreased and biomass burning sources became the major source of BC in the Sanjiang Plain.

From the 1960s to the 1990s, nearly 60% of the wetlands in Sanjiang Plain disappeared and 70% of the disappeared wetlands were converted into farmland (Wang et al., 2009). Fire was a useful tool to reclaim the wetlands and widely used from the 1960s–1990s, as a result, large amounts of BC were emitted and biomass burning became the major source of BC, resulting in the highest BC fluxes during the last 150 years. In 1996, the government started to protect the wetland ecosystem in the Sanjiang Plain (Wang et al., 2009) by implementing the restriction of using fire to reclaim lands. The BC fluxes from biomass burning decreased as a result. On the other hand, after the 1990s, with the local economy developing, BC emitted from industry and transportation sources increased and became the major sources of BC in the Sanjiang Plain. Increase in BC fluxes from industry and transportation in the region were parallel with the China BC emission trend (Fig. 5). In the 2000s, with environment-friendly technology developing, BC emission from national and regional industry sources started to decrease (Bond et al., 2007) and major BC sources were from transportation sources and biomass burning sources. In the 2000s, BC fluxes were contributed by mixed sources and the transportation source became the major source for the first time. BC sources changed from simple sources before the 1980s to mixed sources in the present and the government should control the regional BC emission by controlling BC emission from all types of sources.

Although the way of biomass burning (e.g. occurs in fields, cooking) and fossil fuels combustion (e.g. liquid fuels consumed in industry or transportation) are still unable to separate at this moment, regional economic developing and human activities were confirmed as the major factors that control the BC sources in Sanjiang Plain during the last 150 years, especially after the 1950s. At the end of the 1950s, the environment-unfriendly industry development produced a great amount of BC and was the major factor that caused BC fluxes increased obviously. High amount of BC produced from reclaiming farmlands during the 1960s–1990s produced was the major factor that led BC fluxes increased obviously during this period. After the 1990s, BC produced from biomass burning and industry sources decreased, and transportation became the major BC source and led BC fluxes increased gradually from the end of 1990s to present.

5. Conclusions

PAHs and BC were co-emitted from biomass incomplete burning and fossil fuels consumed, thus, PAH components calculated by discriminant analysis are helpful for identifying pyrolysis sources. Although slight differences of δ^{13}C-BC from pyrolysis sources lead δ^{13}C-BC could not be used for quantifying the sources of BC from fossil fuels or biomass burning, δ^{13}C-BC could be used for evaluating whether the pyrolysis sources identified by PAH components similar with those identified by δ^{13}C-BC. Based on PAH components and δ^{13}C-BC, historical BC sources in Sanjiang Plain during the last 150 years were identified and verified. BC was primarily produced from biomass incomplete burning in the Sanjiang Plain, especially from reclaiming farmlands during the 1950s–1990s. However, the environment-unfriendly industry development also produced a great amount of BC emitted into the atmosphere and deposited into the soil at the end of the 1950s. And transportation became an important BC source after the 1990s, because the region reclaiming decreasing and environment-friendly industry developing led BC emitted from other two sources decreased. Overall, BC sources in the Sanjiang Plain were mixtures of incomplete combustion of biomass and fossil fuels.

Acknowledgments

The authors gratefully acknowledge the assistance of the Analysis and Test Center of Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. The authors acknowledge two anonymous reviewers for their comments on this paper, and also acknowledge Stefan Doerr for his comments on the early version of this paper. Financial support was provided by the National Key Research and Development Project (No. 2016YFA0602301) and the National Natural Science Foundation of China (No. 41571191; 41701217; 41620104005).

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